

# CATALYTIC REACTIONS OF ALIPHATIC ALCOHOLS OVER THORIUM OXIDE

By  
JOHN WALLIS LEGG

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## I. INTRODUCTION AND HISTORICAL REVIEW

Extensive investigations have been made correlating the chemical properties of catalysts and their activity in promoting reactions in the gas phase. A number of purely chemical theories have been proposed, one of the most notable being the "multiplet theory" of Balandin (1). He proposed that, because of its chemical nature, a catalyst possesses certain sites which cause reactant molecules to be arranged in such a way as to promote the breaking of certain bonds and the formation of others. Although much of Balandin's theory is almost certainly in error, notably the absence of chemisorption, such chemical properties as crystal structure and the availability of bonding electrons at the surface are important factors in determining the activity of a catalyst.

Although early investigators realized that the physical properties of the catalyst surface were probably important, only in relatively recent years have methods been made generally available to the chemist for investigation of these physical properties. Thus, alcohols have been reacted over thorium oxide by a number of investigators since 1908 when Sabatier and Maihle (2) effected the decomposition of ethanol, but often the data are difficult to correlate, since little is known of the physical properties of the catalysts used. One of the purposes of the present investigation



has been to correlate one physical property, the surface area, with the reactivities of a number of alcohols over different thorium oxide catalysts.

It is well known that thorium oxide, or thoria, effects both the dehydration and dehydrogenation of alcohols. Adkins (3) was probably the first to propose that, over catalysts which promoted both reactions, the physical properties of the catalyst surface affected the relative rates of the two reactions and that these reactions occurred on different sites.

Hoover and Rideal (4), reacting ethanol over thoria which had been prepared by precipitation from thorium nitrate, found approximately equal rates for the two reactions. Experiments with water vapor as a poison showed that adsorption of water decreased the dehydration to a greater extent than the dehydrogenation. They concluded that there were separate partial surfaces for each reaction.

G. M. Schwab (5) extended this idea in making a proposal as to the nature of each of these partial surfaces. His investigations of the decomposition of ethanol and formic acid over thorium oxide, as well as a number of other oxides, led him to conclude that "the active centers for the dehydration of ethanol and formic acid are identical, and the same is true for the centers of dehydrogenation." Treatment of the catalyst such as prolonged heating, which decreased the number of pores, crevices and channels, decreased considerably the dehydration and increased slightly the dehydrogenation. In electron microphotographs, at 100 angstroms resolution, of strongly dehydrating and strongly

dehydrogenating catalysts the former appeared compact while the latter resembled a loose powder. Thus, Schwab reasoned, the pores in the dehydrating catalyst were of the order of molecular size. He proposed that dehydrogenation occurs on the flat surfaces of the catalyst while dehydration occurs in pores and crevices of such size that the reactant molecule is attached to opposing sides.

If Schwab's proposal is correct, an increase in size of the reactant molecule should have an adverse effect on the dehydration reaction. In the investigation described in this dissertation, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol have been reacted over thoria in an effort to determine this effect of molecular size.

Little work has been done until recently on the reactions of the higher alcohols over thoria. Winfield (6) reacted 2, 3-butanediol over a number of catalysts in an effort to obtain methyl vinyl carbinol and then butadiene in a second dehydration. Alumina, quartz chips,  $B_2O_3$ , and  $BeO$ , among others, yielded methyl ethyl ketone. Thoria alone effected the reaction with the less favorable free energy change, that to methyl vinyl carbinol. Winfield's catalysts prepared from thorium oxalate showed much more reactivity than those from the hydroxide. Investigations in this laboratory (7) have shown that thoria prepared from the oxalate has a much higher surface area than that from the hydroxide, especially as prepared by Winfield.

In a recent article Lundeen and Hoozer (8) point out that Winfield's production of methyl vinyl carbinol is just one

example of the remarkably specific nature of thoria as a dehydration catalyst. Whereas alumina (9) and numerous other metal oxides (10) yield mixtures rich in the 2-olefin upon dehydration of secondary 2-alcohols, thoria and other oxides of group III B catalyze the dehydration of the 2-alcohols to yield the 1-olefin almost exclusively. In contrast to the carbonium ion and oxonium ion mechanisms usually proposed for the elimination of water over alumina (9) (10), Lundeen and Hoozer propose a concerted mechanism for the reaction over thoria, in which the elements of water are eliminated as the olefin is formed, in a single step. A hydrogen from the methyl group alpha to the hydroxyl carbon, instead of a hydrogen from the alpha methylene group, attaches to the surface and is eliminated with the hydroxyl group. To attach a hydrogen from the methylene group, the molecule would have to overcome eclipsing interactions and bring a larger portion of the molecule nearer the surface. The concerted mechanism is similar to that proposed by Schwab (5), but these investigators do not discuss the porosity of the catalyst.

Although alumina and similar catalysts quite easily promote the dehydration of primary alcohols to ethers (10), dehydration to ether does not occur over thoria (11) (12).

Most investigators have found that secondary alcohols dehydrate much more readily than do the corresponding primary alcohols and that, in general, the higher primary alcohols dehydrate more readily than those of lower molecular weight. Bork and Tolstopyatowa (13), in working with alumina, put the order as 2-propanol > 2-butanol > 2-methyl-1-propanol > 1-butanol >

1-propanol > ethanol; the same sequence was obtained by Freidlin and Levit (14) using as a catalyst tricalcium phosphate. As will be discussed later, these results are in contrast to those found in the present investigation of thoria.

At the present time, no single comprehensive mechanism of the reactions of alcohols over thoria has been proposed. Any mechanism would have to explain both dehydration and dehydrogenation, including the favoring of one reaction over the other with a given catalyst, the non-formation of ethers, and the specificity of the production of 1-olefin to that of 2-olefin from secondary 2-alcohols.

## II. EXPERIMENTAL METHODS

### A. The Catalyst

#### 1. Preparation

All of the catalysts were prepared by precipitation of thorium hydroxide from a solution of thorium nitrate by the rapid pouring of a more-than-theoretical amount of concentrated ammonium hydroxide into the solution. Some of the thorium nitrate was obtained from the Fisher Scientific Company, the rest from the J. T. Baker Chemical Company. The source of the ammonium hydroxide was the Allied Chemical and Dye Corporation.

After precipitation the hydroxide was filtered and washed with distilled water; the number of washings and volume of each wash varied between batches. The precipitate was dried overnight at 120°, <sup>1</sup> ground to a 200 mesh, and heated under vacuum at 300° for two hours. Pellets one-half inch in diameter and one-sixteenth to one-eighth inch thick were made at a pressure of about 92,000 pounds per square inch; these were usually cut in half before introduction into the reaction tube. The pelleted catalyst was then activated by heating under vacuum at 600° for at least four hours. The heating at 300° was done to remove enough water so that the pellets did not crack or crumble during the final activation.

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1. All temperatures are in degrees centigrade.



a. Catalyst I

One-hundred twenty grams of  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  was dissolved in 1,500 milliliters of water and 150 milliliters of concentrated ammonium hydroxide rapidly poured in with stirring. The mixture was suction filtered and the precipitate washed, while still on the filter paper, until the filtrate had a pH of seven, as determined with pHDrion paper. After drying and pelleting, the catalyst was activated for four hours.

b. Catalyst II

Eighty grams of  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  was dissolved in 100 milliliters of water and 60 milliliters of concentrated ammonium hydroxide added by rapid pouring with stirring. The mixture was suction filtered and washed with five portions, 500 milliliters each, of water while the precipitate was still on the filter paper. The final pH of the filtrate was six. After drying and pelleting, the catalyst was activated for four hours.

c. Catalyst III

Ninety grams of  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  was dissolved in 1,100 milliliters of water and 110 milliliters of concentrated ammonium hydroxide poured in rapidly with stirring. After filtration the precipitate was removed from the filter paper and thoroughly stirred with 500 milliliters of water. The precipitate was allowed to settle and the supernatant liquid pulled off with an aspirator. Another 500 milliliters of water was added; the process was repeated until 7,500 milliliters of water had been used and the pH was seven. After the usual drying and pelleting, the catalyst was activated for four hours.

#### d. Catalyst IV

One-hundred twenty grams of  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  was dissolved in enough water to make 525 milliliters of solution, then 300 milliliters of concentrated ammonium hydroxide was added by rapid pouring with stirring. After suction filtration the precipitate was removed from the filter paper and stirred with 400 milliliters of water. This mixture was then filtered and the process repeated until a total of 2,000 milliliters of wash water was used. This catalyst was activated a total of twenty-five hours prior to introduction into the reaction vessel.

#### e. Catalyst V

Ninety grams of  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  was dissolved in 1,100 milliliters of water and 110 milliliters of concentrated ammonia rapidly poured in with stirring. The resulting mixture was suction filtered. After being removed from the filter paper the precipitate was stirred with 400 milliliters of water. This mixture was filtered and the process repeated until a total of 2,000 milliliters of wash water was used. Catalyst V was activated for a total of twenty-nine hours prior to introduction into the reaction tube.

#### f. Catalyst VI

One-hundred twenty grams of  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  was dissolved in enough water to make 525 milliliters of solution and 300 milliliters of concentrated ammonium hydroxide was added by rapid pouring with stirring. The resulting mixture was filtered and the precipitate removed from the filter paper. It was stirred with 400 milliliters of water and this mixture filtered. This

was repeated four times for a total wash volume of 1,600 milliliters. Prior to introduction into the reaction tube catalyst VI was activated a total of twenty-nine hours.

Catalyst I was activated in a Vycor tube, a portion saved for surface area measurements and 20.0 grams placed in the reaction tube. Pellets of catalyst II and III were introduced into the reaction tube prior to activation, the final activation taking place in the reaction tube itself. The portion for surface area measurements was activated separately.

It became apparent during runs with the first three catalysts that it would be desirable to reactivate the catalysts at times between runs. However, it has been shown (7) that this reactivation decreases the surface area of the catalyst. This decrease is rapid at first; after several hours activation the surface area decreases less drastically with heating. In order to be able to reactivate without changing appreciably the surface area of the catalyst, catalysts IV, V and VI were each activated for several hours prior to introduction into the reaction chamber, surface areas being determined after each few hours activation until little change was noted with further heating.

## 2. Surface areas

The nitrogen surface areas, in square meters per gram, of the six catalysts used, determined by the B.E.T. method (15) (18), are listed below. The activation time is the total time of activation prior to the first reaction run over the catalyst.

Catalyst	Activation Time	Surface Area
I	4 hours	1.2
II	4 hours	6.5



Catalyst	Activation Time	Surface Area
III	4 hours	17.8
IV	26 hours	34.4
V	30 hours	12.2
VI	30 hours	28.9

### 3. Reaction Runs

#### 1. Purification of alcohols

The ethanol was obtained from the Union Carbide Chemicals Company, the 2-propanol from the Mallinkrodt Chemical Works, the 1-propanol and 1-butanol from the Fisher Scientific Company and the 2-butanol from Eastman Organic Chemicals. In order to remove aldehyde impurities and water all the alcohols except 2-butanol were stored from several days to several weeks over calcium oxide which had been heated at 800° for several hours. They were then distilled until no impurity could be detected with a vapor phase chromatograph constructed in this laboratory; two distillations were usually sufficient. The reagent grade 2-butanol was used as obtained; no impurities could be detected in this material with the chromatograph.

#### 2. Reaction apparatus

The flow system shown schematically in Figure 1 was used for all reaction runs except for some of the initial trial runs. It permitted the passage of alcohol over the catalyst at various flow rates and temperatures and the collection of the liquid and gaseous products.

The reaction vessel was made of a Vycor tube 81 centimeters long with an inside diameter of 22 millimeters. A Vycor thermocouple well extended through the top of the reaction tube to the

1. Reactant Reservoir
2. Flowmeter
3. Needle valve
4. To vacuum pump
5. To nitrogen tank
6. To manometer
7. Thermocouple well
8. Reaction tube
9. Furnace
10. First collection flask
11. Second collection flask
12. Gas sampling bulb
13. Wet Test Meter

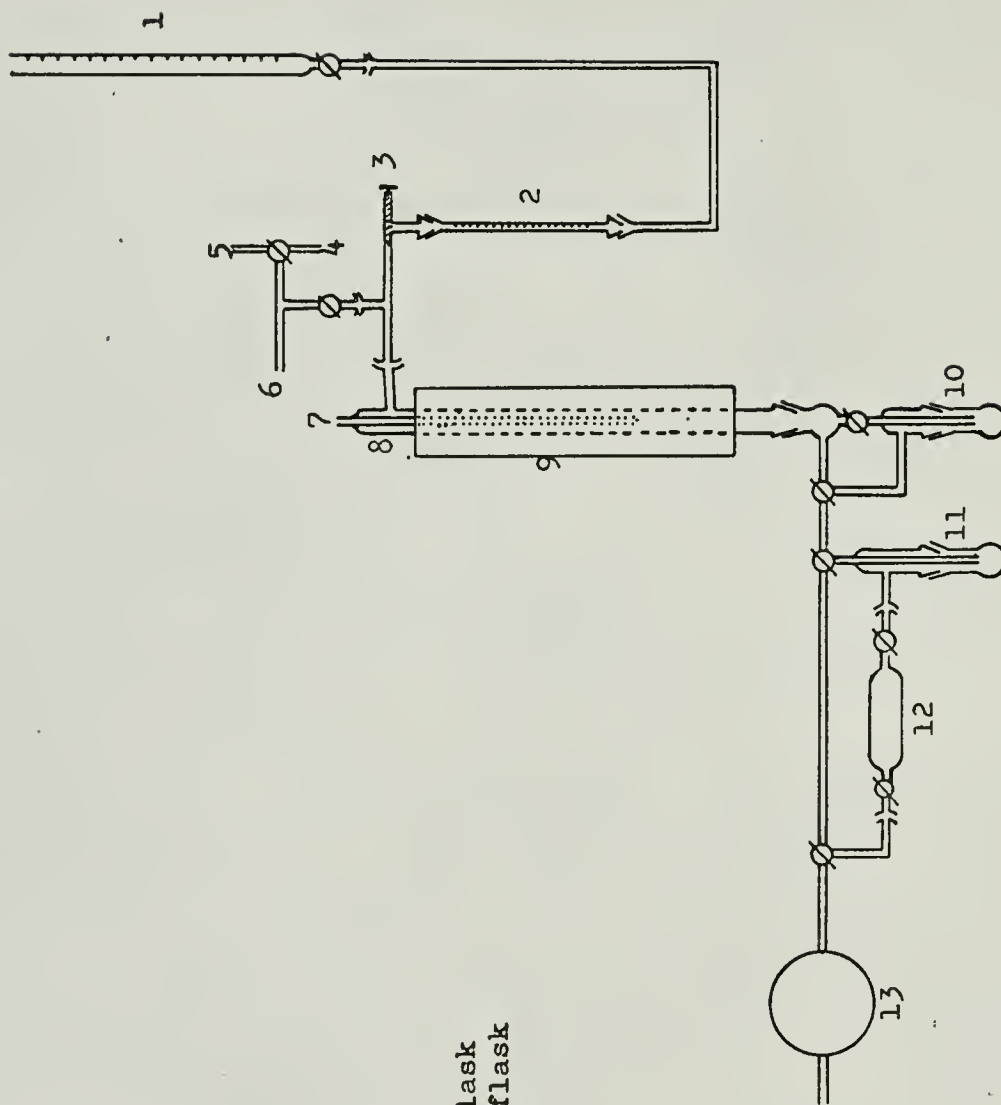


Figure 1. Reaction Apparatus

center of the catalyst bed. The catalyst was supported by a perforated porcelain disc which in turn was supported by a spacer tube resting on indentations in the reaction tube. Reactant alcohol entered the reaction tube through a sidearm near the top of the reaction tube.

The furnace, a porcelain tube with three separate heating coils and appropriate insulation, has been described by Schmidt (12). The middle coil, which surrounded the catalyst bed, was connected through a Variac to a model 402 Wheelco Proportioning Capacitrol. The chromel-alumel thermocouple which was used in conjunction with the Capacitrol was inserted in a thermocouple well outside the porcelain tube to a point just outside the catalyst bed. Temperature control above and below the catalyst was maintained by manual manipulation of two Variacs to which the top and bottom coils were connected.

A second thermocouple was inserted into the reaction tube thermocouple well to the center of the catalyst bed. The reaction temperature was then read from a second Wheelco Capacitrol; this second Capacitrol was not used as a regulating device but simply as a meter. The temperature could be controlled and determined to within two degrees in the range of reaction temperatures used, 315° to 420°.

The reactant alcohol was contained in a graduated reservoir situated above the reaction vessel. From the reservoir the alcohol flowed through a Fischer and Porter Precision Bore Flowrater No. 08-150 and a Fischer and Porter glass and teflon needle valve which regulated the rate of flow. Between the needle valve and

the reaction chamber was placed a "T" with vacuum stopcock and lines to a manometer, vacuum pump and nitrogen tank.

Vycor chips were always packed above the catalyst to a height of about seven inches. By regulation of the voltage to the top coil in the furnace the temperature of these chips could be made the same as that of the catalyst bed, as determined by raising the thermocouple in the reaction tube well. Thus the reactant alcohol flowed onto these chips, evaporated, and was heated to reaction temperature prior to its contact with the catalyst.

Upon leaving the reaction tube the reaction products and unreacted alcohol passed into the first product collection flask. Here all materials which were liquids at room temperature were trapped out. The remaining products passed through a second collection trap which was cooled with a dry ice-acetone slush. The remaining gases passed through a gas sampling bulb and on through a Wet Test Meter, manufactured by the Precision Scientific Company, which measured the total volume of these gases. The Wet Test Meter was calibrated by passing known volumes of nitrogen through it at approximately the same pressure differentials as those which existed during reaction runs.

### 3. Procedure for a series of reaction runs

Twenty grams of pelleted catalyst was placed on the perforated disc, about seven inches of preheater chips packed on top of the catalyst, and the reaction tube placed in the furnace.

Catalysts I, II and III were activated for four hours after the reaction tube was in place. Although catalysts IV, V and VI were activated before being placed in the reaction tube, they were

each reactivated for one hour after placement to remove water adsorbed during the transfer.

The three heaters were turned on and the preheater and catalyst bed allowed to come to reaction temperature under an atmosphere of dry nitrogen. Alcohol was introduced, the flow rate adjusted to that desired, and the system allowed to equilibrate for ten to thirty minutes before an actual run was started.

After equilibration, the time, temperature, volume of alcohol in the reservoir and wet test meter reading were recorded and the two collection flasks changed as quickly as possible. The alcohol flowed for thirty minutes to two hours until at least ten milliliters had passed into the reaction tube, with periodic checks on the flow rate and reaction temperature. To conclude a run, final readings were made and the flasks again quickly changed.

Another period of equilibration at a new flow rate preceded the next run. Usually four runs were made at a given temperature, three at different flow rates; the fourth run duplicated the first as a check on any change in catalyst activity.

After a series at a given temperature was completed, the unreacted alcohol and reaction products still in the reaction tube were pumped out and the catalyst heated under vacuum about thirty minutes at the reaction temperature.

A number of times two series of runs, at different temperatures, were made in a single day. When this was done, the alcohol continued to flow after the first series was completed while the system was coming to thermal equilibrium at the new temperature.



#### 4. Analysis of reaction products

##### a. Liquid products

A vapor phase chromatograph, described by Moreland (15), was used for all quantitative and most qualitative analyses of liquid products. Attempts were made to analyze reaction products from 1-propanol using nuclear magnetic resonance (NMR) spectroscopy, but vapor phase chromatography proved more satisfactory. The chromatograph column, twenty feet of one-fourth inch copper tubing, was packed with F. and M. Scientific Corporation's 5 per cent Carbowax 1500 on Haloport F.

During the analysis of ethanol, 2-propanol, and 1-butanol, the column temperature was 95° and the pressure of the helium carrier gas was seven pounds per square inch. The temperature was 60° and the helium pressure was five and one-half pounds for the analysis of 1-propanol and 2-butanol reaction products.

Most of the reaction products were identified by comparing retention times on the column to those of known compounds or by adding a small amount of the known to the product mixture and noting which peak increased in size. This identification is discussed in more detail in the Appendix.

Although trace amounts of any number of reaction products are to be expected in catalytic reactions, no more than 1 per cent of components other than the initial dehydration and dehydrogenation products were obtained with ethanol, 2-propanol or 2-butanol. However, 1-propanol and 1-butanol yielded in appreciable amounts products, one for each alcohol, which were not expected from simple dehydration or dehydrogenation.

In order to identify these two components, reaction mixtures of both 1-propanol and 1-butanol were distilled using a spinning band column. The 1-propanol product had a boiling point in the range 114°-117° and the 1-butanol product boiled in the range 142°-145°. Infrared and NMR spectra were obtained for both products. It was concluded from this evidence that the 1-propanol product was 3-pentanol and the 1-butanol product was 4-heptanone.

Solutions of known composition were made of each of the alcohols and known reaction products, chromatograms were made of each solution, and relative areas of the peaks were determined using a planimeter.

It was found, in working with numerous compounds, that the relative areas of two peaks on a chromatogram were very nearly the same as the relative weights of the two components in solution. For example, a 20 per cent by weight (39 mole per cent) solution of water in ethanol produced a chromatogram on which the water peak was 21.5 per cent of the total area. This correlation improved as the ratio of the molecular weights of the two components approached unity.

In view of this, calibration curves were made of the alcohols and water and the amounts of the other products calculated assuming that peak area percentages were the same as weight percentages. Subsequent analyses of known solutions checked within experimental error.

#### b. Gaseous products

Time-of-flight mass spectra were obtained on samples of gas from one run with 1-propanol and one with 1-butanol. In both

cases the gases had passed through two condensation traps so that practically all materials condensable at dry ice temperatures had been removed.

The sample from 1-butanol was determined to have 73 per cent hydrogen with little air contamination. That from 1-propanol had 46 per cent hydrogen with considerable air contamination. Although an exact determination was not made for other species, it could be determined that at least the major portion of the remaining gas was carbon monoxide in each sample.

An infrared spectrum of the olefin produced from 2-butanol was obtained to ascertain whether this was 1-butene or 2-butene. In agreement with the results of Lundeen and Hoozer (8), the spectrum matched a standard spectrum of 1-butene.



### III. PRESENTATION OF DATA

#### A. Explanation of Tables

In Tables I through V are recorded the operating conditions and results of all the runs for which reliable data were obtained. Runs 1 through 46 with ethanol were exploratory and are not included; a few other runs are omitted because circumstances were such as to make the results unreliable.

In the third column the reaction temperature is that of the catalyst bed in degrees centigrade. The reciprocal flow rate is listed as minutes per mole of alcohol. This was calculated by dividing the time interval of a run by the number of moles of reactant which left the reservoir during that time, as determined from the volume of alcohol feed and known densities.

The mole per cent dehydration was determined as described in section II-B-4. The per cent dehydrogenation of 2-propanol and 2-butanol was obtained by determining chromatographically the amount of ketone produced. Per cent conversions of 1-propanol to 3-pentanol and 1-butanol to 4-heptanone were calculated from Wet Test Meter gas volumes, assuming ideality. Numerous cross-checks were made between chromatographic data and data obtained from gas volumes. Examples are given in the Appendix.

Although small amounts of acetaldehyde were detected during runs with ethanol, dehydrogenation was seldom over 1 per cent and

TABLE I  
REACTION RUNS WITH ETHANOL

Run No.	Catalyst	Reaction Temperature	<u>1</u> Flow Rate	Per Cent Dehydration to Ethylene
47	I	373	792	30
48	I	373	505	18
49	I	383	814	21
50	I	383	435	12
51	I	383	253	9
52	I	383	441	13
53	I	400	736	35
54	I	400	410	22
55	I	400	172	9
56	I	400	371	18
57	I	400	182	37
58	I	417	441	35
59	I	417	800	44
60	I	417	155	17
61	I	417	434	32
62	I	426	1003	63
63	I	426	410	37
64	I	426	541	43
65	I	427	138	17
66	I	426	260	26
67	I	426	730	48
68	I	426	394	40
69	I	426	583	48
70	I	426	714	47
71	I	426	279	25
72	I	426	545	40
73	I	426	581	41
74	I	426	589	41
75	I	426	542	40
76	I	418	417	36
77	I	418	247	22
78	I	400	403	26
79	I	400	722	32
80	I	400	416	18
81	I	418	832	37
82	I	426	759	31
83	I	426	390	21
84	I	426	532	35
85	I	426	228	19

TABLE I - Continued

Run No.	Catalyst	Reaction Temperature	<u>l</u> Flow Rate	Per Cent Dehydration to Ethylene
86	II	365	756	46
87	II	365	359	33
88	II	365	200	16
89	II	365	575	40
92	II	384	134	29
93	II	384	496	60
94	II	397	327	51
95	II	396	153	31
96	II	396	562	62
97	II	395	314	43
98	II	395	335	44
99	II	395	331	47
100	II	348	335	21
101	II	348	217	15
102	II	348	603	18
103	II	348	331	13
104	II	395	344	46
105	II	387	327	37
106	II	387	595	49
107	II	387	171	27
108	II	387	328	37
109	II	385	469	48
110	II	395	438	56
111	II	365	422	28
112	II	384	422	42
113	III	384	437	51
114	III	384	196	28
115	III	384	592	60
116	III	384	206	27
117	III	360	382	20
118	III	360	446	24
119	III	395	438	52
120	III	395	432	50
121	III	395	190	34
122	III	395	627	60
123	III	395	192	30
125	III	365	487	24
126	III	365	480	26
127	III	365	184	14
128	III	365	775	34
129	III	365	489	24
130	III	385	541	45

TABLE I - Continued

Run No.	Catalyst	Reaction Temperature	<u>l</u> Flow Rate	Per Cent Dehydration to Ethylene
131	III	385	189	26
132	III	385	740	50
133	III	385	499	39
134	III	385	486	40
135	III	385	503	41
136	III	385	489	39
137	III	385	466	38
138	III	385	487	39
139	III	385	510	40
140	III	385	506	38
142	III	385	517	38
143	III	385	525	39
144	III	385	487	35
145	III	385	484	31
147	IV	385	446	78
148	IV	385	206	59
149	IV	385	308	67
150	IV	385	476	75
152	IV	385	435	51
153	IV	385	208	44
154	IV	385	364	50
156	V	360	323	39
157	V	360	214	32
158	V	360	436	46
159	V	360	348	37
161	V	345	329	28
162	V	345	443	31
163	V	345	211	19
164	V	345	336	22
165	V	385	322	51
166	V	385	205	39
167	V	385	444	56
168	V	385	319	50
170	V	365	323	31
171	V	365	443	42
172	V	365	207	28
173	V	365	324	34
174	V	360	317	24
175	V	360	331	23
176	V	365	338	27
177	VI	325	322	22
178	VI	325	433	24

TABLE I - Continued

Run No.	Catalyst	Reaction Temperature	<u>l</u> Flow Rate	Per Cent Dehydration to Ethylene
179	VI	325	233	17
180	VI	325	312	21
181	VI	345	305	29
182	VI	345	215	23
183	VI	345	389	34
184	VI	345	307	27
185	VI	365	320	44
186	VI	365	421	50
187	VI	365	202	32
188	VI	365	315	41
189	VI	325	313	21
190	VI	345	363	17
191	VI	345	350	14
192	VI	345	342	18

TABLE II  
REACTION RUNS WITH 2-PROPANOL

Run No.	Catalyst	Reaction Temperature	<u>1</u> Flow Rate	Per Cent Dehydration to Propylene	Per Cent Dehydrogenation to Acetone
2	II	364	992	82	3.2
3	II	364	483	63	3.2
4	II	364	229	42	2.0
5	II	364	463	61	3.2
6	II	352	530	48	2.5
7	II	352	243	32	1.4
8	II	352	845	61	2.8
9	II	352	499	46	2.3
10	II	345	485	40	1.8
11	II	345	762	53	2.5
12	II	345	263	27	1.3
13	II	345	490	39	2.1
14	II	345	490	42	2.2
15	II	352	517	50	2.6
16	II	332	465	32	1.3
17	II	365	474	63	3.2
18	II	375	458	72	3.2
19	II	352	489	48	2.2
20	II	352	2008	85	3.0
21	II	352	473	43	2.0
22	II	352	507	43	2.1
23	II	352	539	57	2.4
24	II	352	908	68	2.8
25	II	345	539	41	1.7
26	II	352	531	49	2.1
27	II	365	585	64	2.8
28	II	352	546	46	2.1
30	V	345	522	54	5.0
31	V	345	384	49	4.4
32	V	345	715	61	5.8
33	V	345	515	52	4.8
34	V	325	475	37	3.3
35	V	325	785	44	4.3
36	V	325	347	32	2.1
37	V	325	508	39	3.0
39	V	315	515	31	2.4
40	V	315	868	39	2.7
41	V	315	385	31	1.9
42	V	315	486	33	2.0

TABLE II - Continued

Run No.	Catalyst	Reaction Temperature	<u>l</u> Flow Rate	Per Cent Dehydration to Propylene	Per Cent Dehydrogenation to Acetone
43	V	345	464	50	4.5
44	VI	315	479	37	1.6
45	VI	315	310	30	0.9
46	VI	315	655	42	2.0
47	VI	315	548	38	1.7
48	VI	325	492	40	1.9
49	VI	325	327	37	1.4
50	VI	325	672	51	2.9
51	VI	325	524	46	1.9
52	VI	345	424	54	2.7
53	VI	345	329	46	1.9
54	VI	345	547	62	3.1
55	VI	345	447	54	2.8
56	VI	315	461	31	1.5

TABLE III  
REACTION RUNS WITH 1-PROPANOL

Run No.	Catalyst	Reaction Temperature	<u>1</u> Flow Rate	Per Cent Dehydration to Propylene	Per Cent Conversion to 3-Pentanol
1	II	365	489	8	5
2	II	365	1323	13	-
3	II	390	519	12	-
4	II	390	1226	18	-
5	II	390	308	-	6
6	II	390	495	16	9
7	II	400	511	15	13
8	II	400	1235	21	-
9	II	400	349	11	9
10	II	400	495	17	14
11	II	420	506	25	22
12	II	420	318	19	14
13	II	420	1171	-	17
14	II	420	465	18	21
15	II	390	456	16	9
16	II	390	1642	30	27
18	V	365	466	14	12
19	V	365	797	17	19
20	V	365	323	12	9
21	V	364	485	14	11
23	V	390	451	22	26
24	V	390	323	18	-
25	V	390	587	25	31
26	V	390	451	26	25
27	V	380	573	20	18
28	V	380	616	19	23
29	V	380	359	17	15
30	V	365	456	11	10
31	VI	365	383	11	7
32	VI	365	545	12	9
33	VI	365	305	9	5
34	VI	385	298	11	9
35	VI	385	651	14	20
36	VI	385	403	11	13
37	VI	400	300	13	14
38	VI	400	491	18	21
39	VI	400	579	23	23



TABLE IV  
REACTION RUNS WITH 1-BUTANOL

Run No.	Catalyst	Reaction Temperature	<u>1</u> Flow Rate	Per Cent Dehydration to 1-Butene	Per Cent Conversion to 4-Heptanone
1	V	365	545	9	
2	V	380	566	13	12
3	V	380	855	14	18
4	V	380	456	13	10
5	V	380	557	14	11
6	V	390	553	21	15
7	V	390	438	17	11
8	V	390	805	24	19
9	V	390	609	22	18
10	VI	365	506	7	8
11	VI	365	391	6	6
12	VI	365	732	12	10
13	VI	365	503	9	8
14	VI	385	497	11	12
15	VI	385	367	11	9
16	VI	385	686	18	16
17	VI	385	497	15	12
18	VI	395	492	18	14
19	VI	395	383	12	12
20	VI	395	694	22	19
21	VI	395	505	16	15
22	VI	365	506	9	5

TABLE V  
REACTION RUNS WITH 2-BUTANOL

Run No.	Catalyst	Reaction Temperature	<u>l</u> Flow Rate	Per Cent Dehydration to 1-Butene	Per Cent Dehydrogenation to 2-Butanone
1	V	325	640	20	8.9
3	V	325	643	21	9.4
4	V	325	855	24	8.6
5	V	325	473	-	5.9
6	V	325	654	-	7.4
7	V	315	702	18	5.1
8	V	315	901	25	6.6
9	V	315	510	11	4.4
10	V	315	710	23	6.0
11	V	345	608	54	7.9
12	V	345	456	47	7.3
13	V	345	330	30	5.4
14	V	325	679	34	6.8
15	VI	315	634	30	5.8
16	VI	315	472	22	5.0
17	VI	315	796	33	6.1
18	VI	315	664	23	5.0
19	VI	325	695	39	5.0
20	VI	325	486	30	4.8
21	VI	325	687	41	5.3
22	VI	325	645	37	4.9
23	VI	300	656	15	2.7
24	VI	300	529	11	2.6
25	VI	300	799	22	2.8
26	VI	300	695	15	2.5
27	VI	315	711	26	4.7

never over 2 per cent. In most cases this was so low that no attempts were made to obtain an exact figure; thus, only conversion to ethylene and water is included in Table I. Since ethylene was not trapped out, the gas volume served as a good check on the dehydration figure determined with the chromatograph.

Propene and butene from dehydration of the higher alcohols could be trapped out and a check made on the dehydration of these alcohols directly. Numerous material balance calculations were made; the error was seldom more than 5 per cent and often considerably less.

Trials with known solutions indicated that the dehydration figures given are accurate to within 5 to 10 per cent of the values listed, the determinations with ethanol and 2-propanol being somewhat better than those with 1-propanol, 1-butanol and 2-butanol.

Although the amount of ketone produced could not be determined to the accuracy implied in Tables II and V, differences of less than one-half per cent were easily detected. Hence, the values are given to the nearest tenth per cent conversion.

## B. Results

### 1. Dehydration

In Figure 2 are plotted, as examples of the type behavior shown by all the alcohols, the results of three series of runs with ethanol over catalyst II. An exception to this behavior was the reaction of 1-butanol over catalyst VI; for this reaction, the best curves through all the points including zero were straight

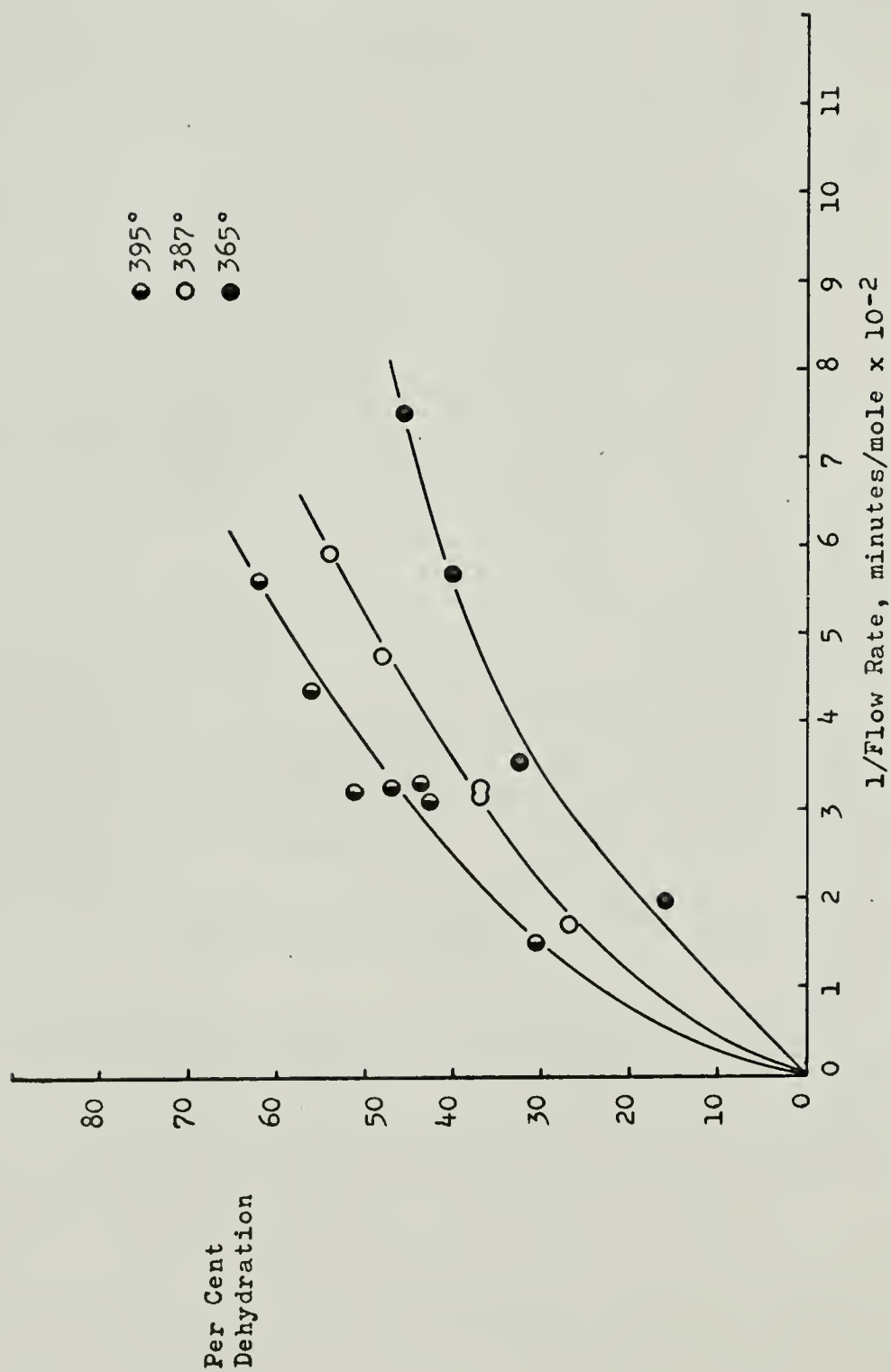


Figure 2. Dehydration of ethanol over catalyst II as a function of reciprocal flow rate

lines. Although this is interesting, no attempts have been made to place any real significance in this deviation from the norm, since the data were collected over such a narrow range of conditions.

Since the temperature range covered was so narrow in every case, no attempts have been made to obtain quantitative temperature correlations, although the qualitative behavior was as expected. A few attempts were made to determine apparent kinetic orders of the reactions. No simple order was found and the data did not justify further attempts.

Catalyst III was accidentally overheated during the initial activation in the reaction tube. In spite of this, a few series of runs were made with ethanol. As anticipated, the conversions were considerably lower than one would expect for the initially measured surface area, although all the runs were consistent within themselves.

Catalyst III was replaced by IV and a series of runs made at 385°. During the initial warm-up period for the second series of runs, the same instrumental malfunction which ruined catalyst III caused the overheating of catalyst IV. A few more runs at 385° verified that the catalyst activity, at least toward ethanol, had decreased considerably and the catalyst replaced.

The behavior of ethanol over different catalysts is illustrated in Figure 3. Since runs over catalyst IV were made only at 385°, most of the plots are for 385°. Runs were not made at 385° over catalyst VI, so plots at 365° over catalysts V and VI are included for comparison of catalyst VI with the others.

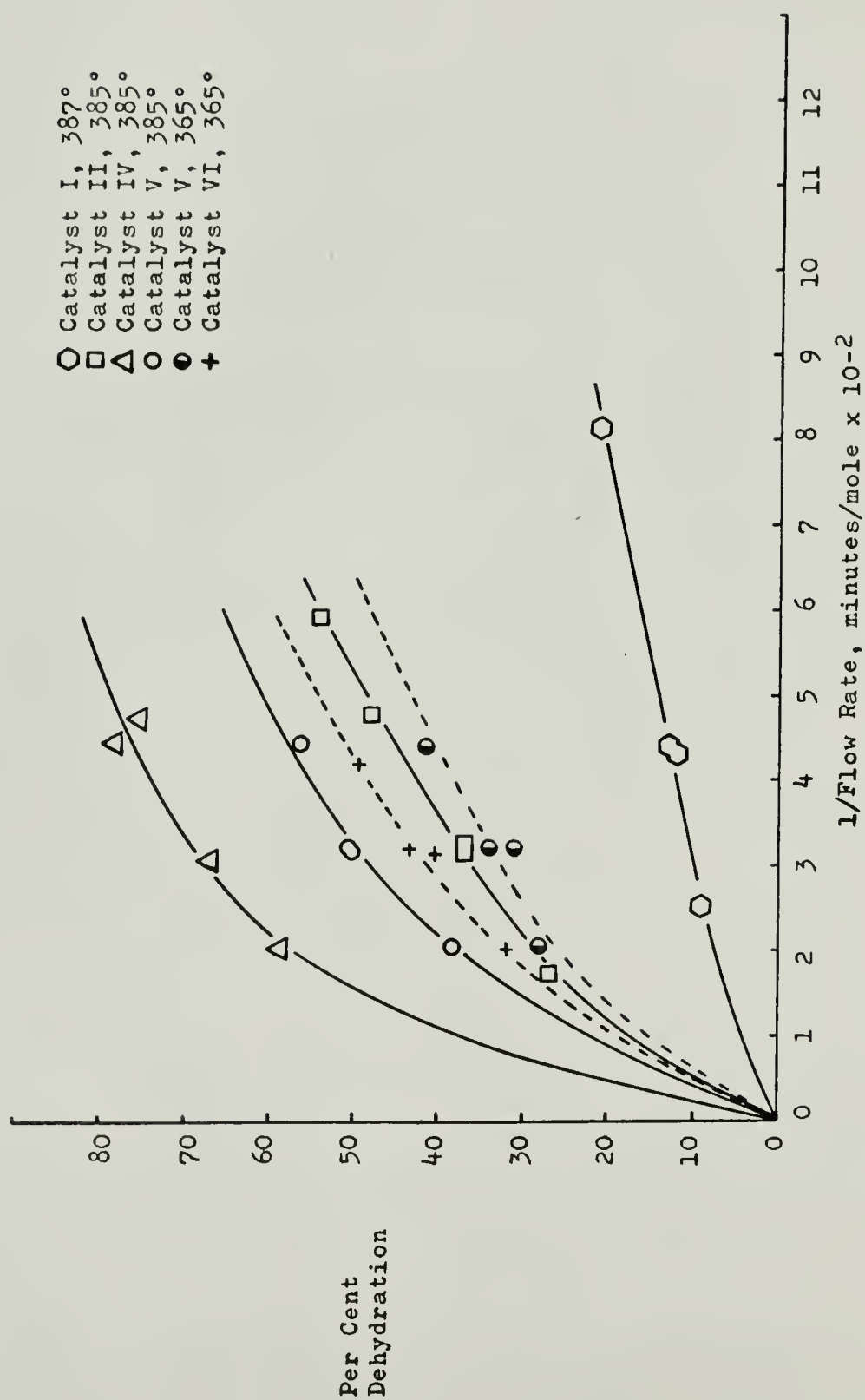


Figure 3. Dehydration of ethanol over different catalysts as a function of reciprocal flow rate

Catalyst III is not included since its surface area at the time runs were made over it was not known.

It is quite apparent that the dehydration of ethanol over thoria is strongly surface area dependent, that the number of dehydration sites for ethanol increases as the surface area increases. The number of sites does not increase linearly with surface area; this point will be discussed more fully later.

In Figures 4 and 5 are illustrated the relative dehydration reactivities of the various alcohols over catalysts V and VI, respectively. It should be pointed out that the plots for the primary alcohols are for runs at 385° or 390° over catalyst V, but for runs at 365° over catalyst VI. The most reliable data for 1-butanol over catalyst V are at 390° while no runs were made with ethanol at temperatures greater than 365° over catalyst VI. The general behavior of each alcohol over each of the two catalysts was essentially the same as that illustrated in Figure 2, with the exception, discussed above, of 1-butanol.

Since ethanol was the first alcohol run over each catalyst, one or more additional runs were made with ethanol after all data-collecting runs had been made to determine any loss of activity during runs with the other alcohols. The activity of catalyst V decreased only slightly during use, but the activity decrease of catalyst VI was almost 40 per cent. This means that the last runs over catalyst VI gave conversions lower than that characteristic of the fresh catalyst. The sequence followed over catalyst VI was: ethanol, 2-propanol, 2-butanol, 1-butanol, 1-propanol. Although corrections for activity decrease could probably be applied



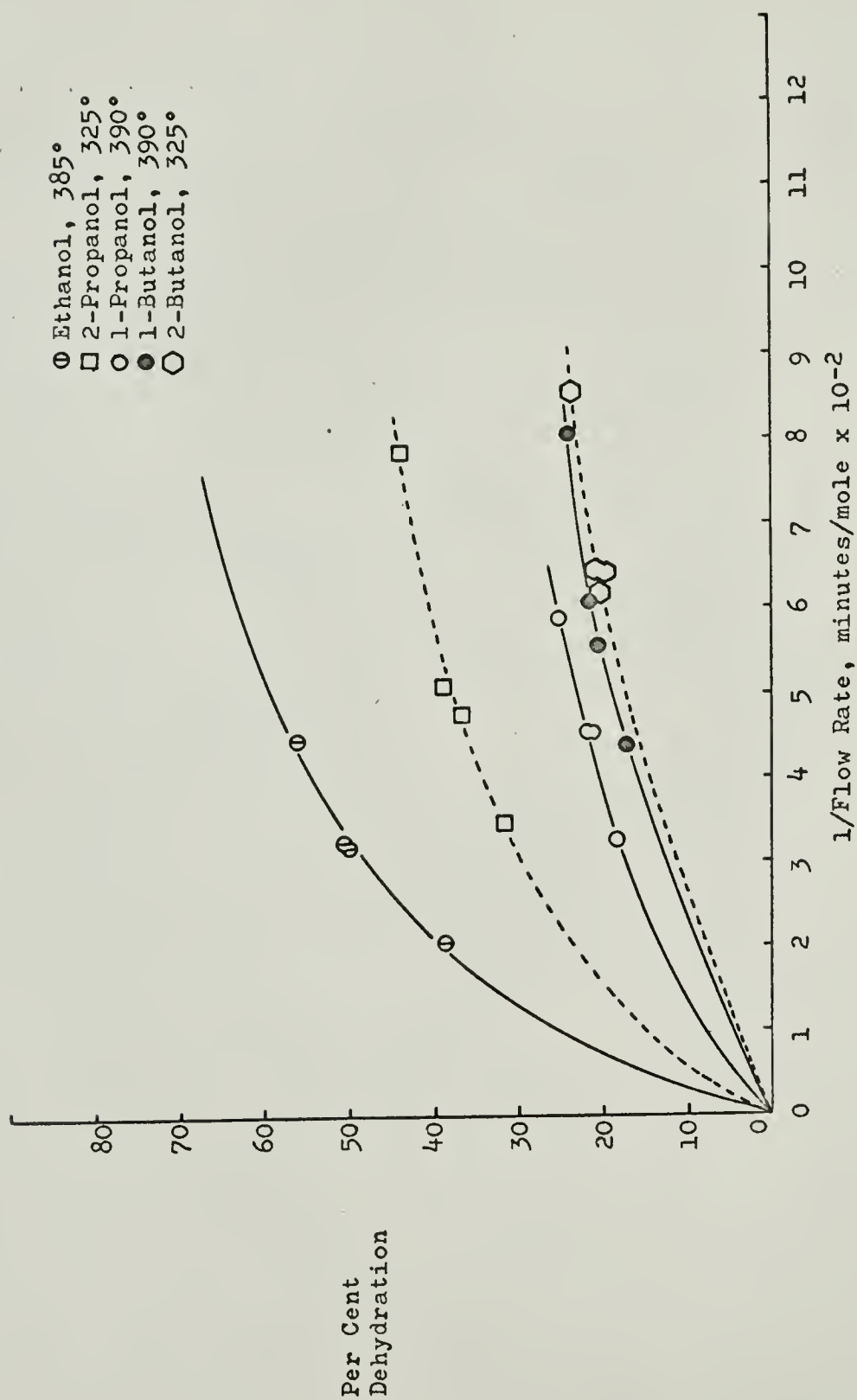


Figure 4. Dehydration of alcohols over catalyst V as a function of reciprocal flow rate



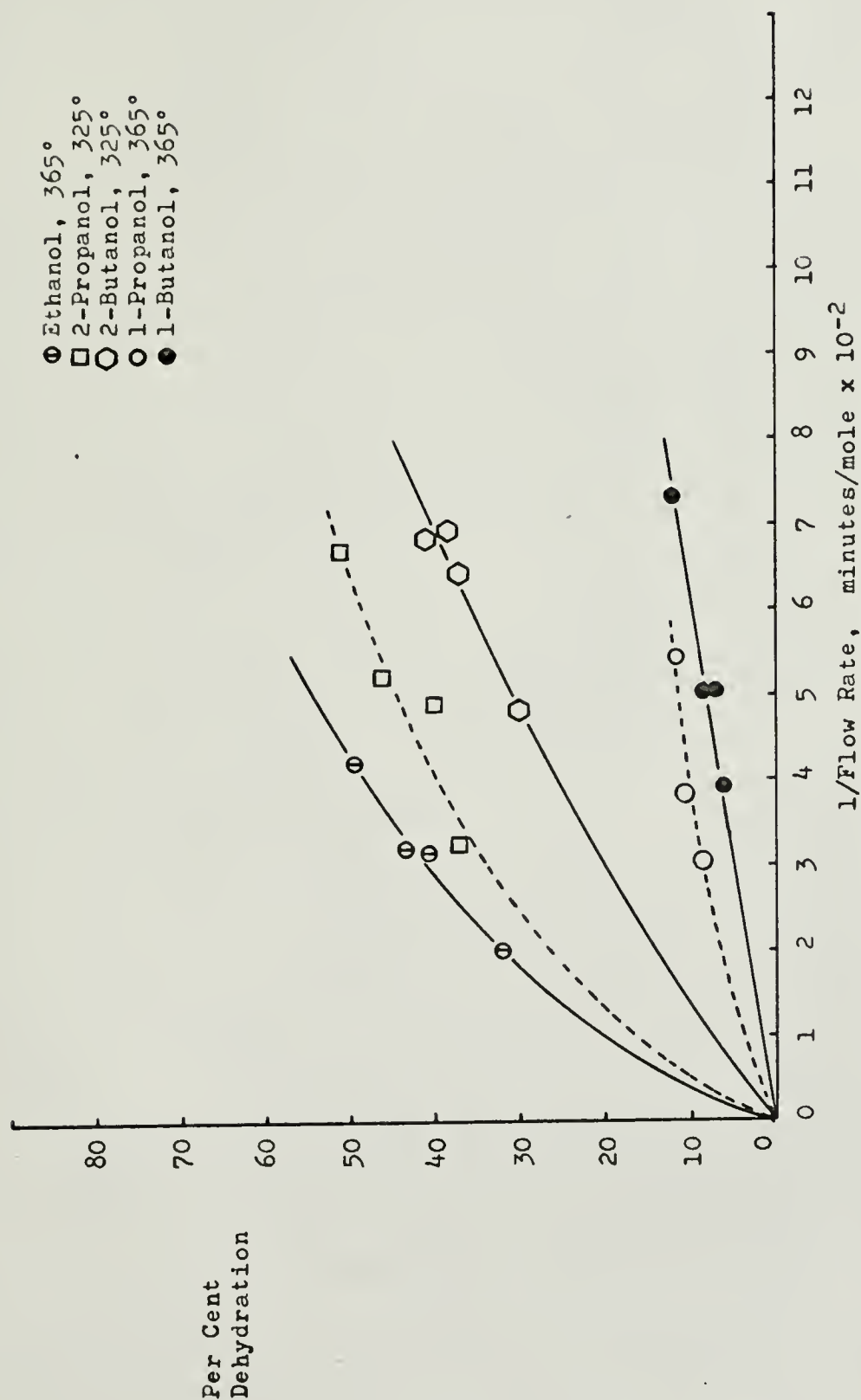


Figure 5. Dehydration of alcohols over catalyst VI as a function of reciprocal flow rate

with reasonable reliability, the uncorrected data are plotted in Figure 5.

In agreement with published results (13) (14) of work with alumina, the secondary alcohols are more reactive than the corresponding primary alcohols. But more important, the dehydration reactivity of the primary alcohols decreases as the molecular size increases, in contrast to these same results.

Perhaps it should be emphasized that 1-propanol was run after 1-butanol over catalyst VI, but that the dehydration of 1-propanol was still higher. Any correction to be applied for a decrease in catalyst activity would tend to make the difference between 1-propanol and 1-butanol even greater, but still leave the reactivity of 1-propanol less than that of ethanol.

Per cent conversion of the three primary alcohols to water and olefin at a reciprocal flow rate of 400 minutes per mole is plotted as a function of surface area in Figure 6. The points for 1-propanol and 1-butanol at a surface area of 28.9 (catalyst VI) are corrected for loss of catalyst activity. As mentioned previously, the per cent dehydration of ethanol increases with an increase in surface area. However, the specific dehydration, or the dehydration per unit area, decreases with a surface area increase. At very low surface areas the specific dehydration is almost constant, but at higher surface areas a doubling of the surface area causes only a fractional increase in dehydration. Above a certain point the dehydration of 1-propanol and 1-butanol exhibits very little dependence on surface area. The difference in the dehydration reactivity over catalysts V and VI was so slight as to be barely detectable.

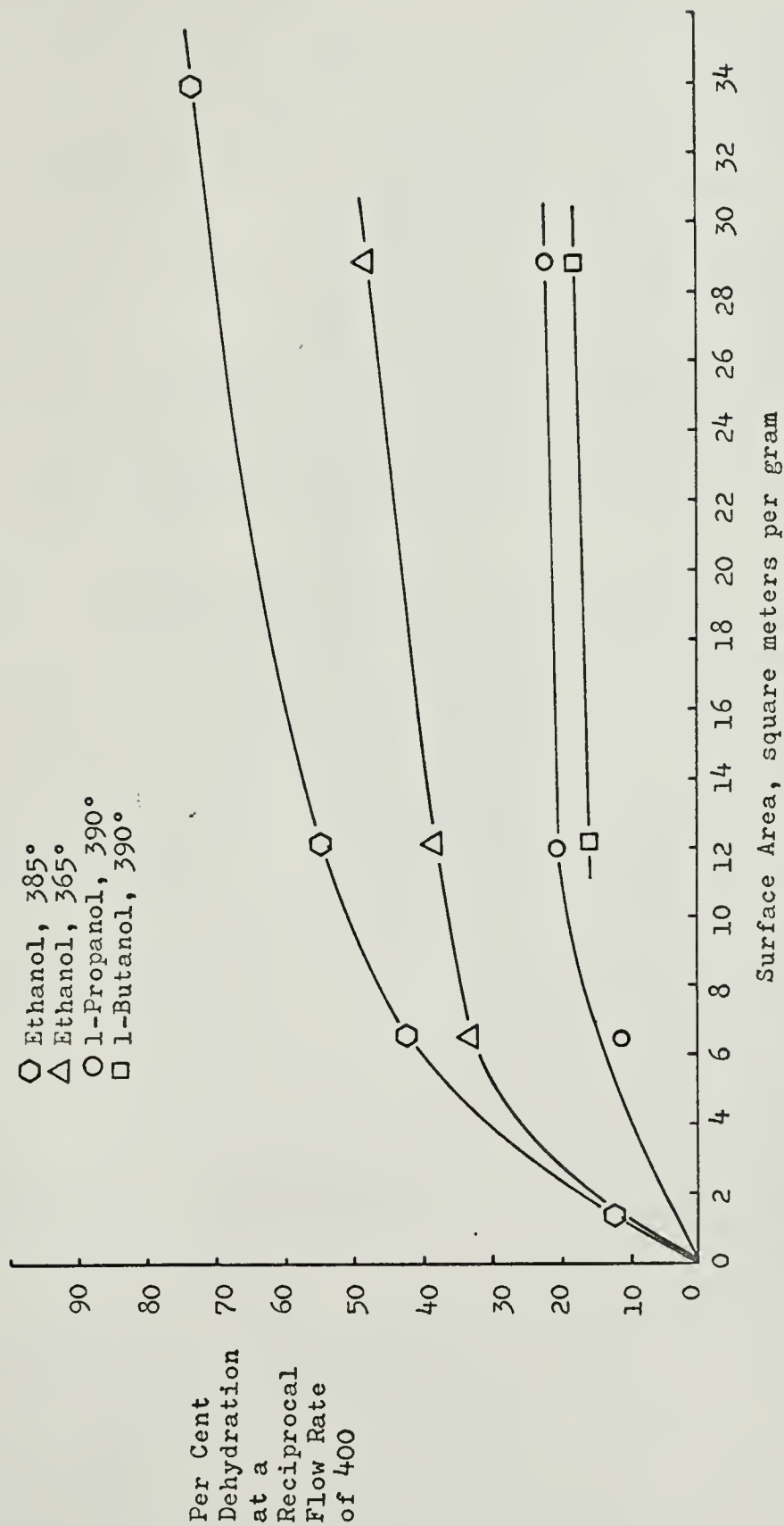


Figure 6. Dehydration of primary alcohols as a function of catalyst surface area

Figure 6 portrays even more emphatically than Figures 4 and 5 the differences in dehydration reactivity of the primary alcohols. An increase in molecular size definitely corresponds to a decrease in activity, with the greatest difference being between ethanol and 1-propanol.

In Figure 7 are plotted dehydration reactivities of the two secondary alcohols as a function of surface area. One of the ethanol curves from Figure 6 is included for comparisons. It is apparent that 2-propanol is more reactive than 2-butanol and that an increase in surface area causes a considerable increase in dehydration of either alcohol. There is a temptation to place significance in the difference in shape between the 2-propanol and the ethanol curves, but, since the runs were made at different temperatures, any conclusions would be subject to doubt.

In summary, the dehydration experiments with the five alcohols permit two primary conclusions: (a) The dehydration reactivities of the alcohols are in the order 2-propanol > 2-butanol > ethanol >> 1-propanol > 1-butanol. (b) An increase in catalyst surface area causes a considerable but non-linear increase in conversion of ethanol, 2-propanol and 2-butanol, but little increase in the conversion of 1-propanol and 1-butanol.

## 2. Dehydrogenation

The only two alcohols which exhibited simple dehydrogenation were 2-propanol and 2-butanol, both reacting to yield ketones and hydrogen.

Although 2-butanol was reacted over only two catalysts, the data are sufficient to permit the observation that 2-butanol dehydrogenates more readily than 2-propanol over thoria.

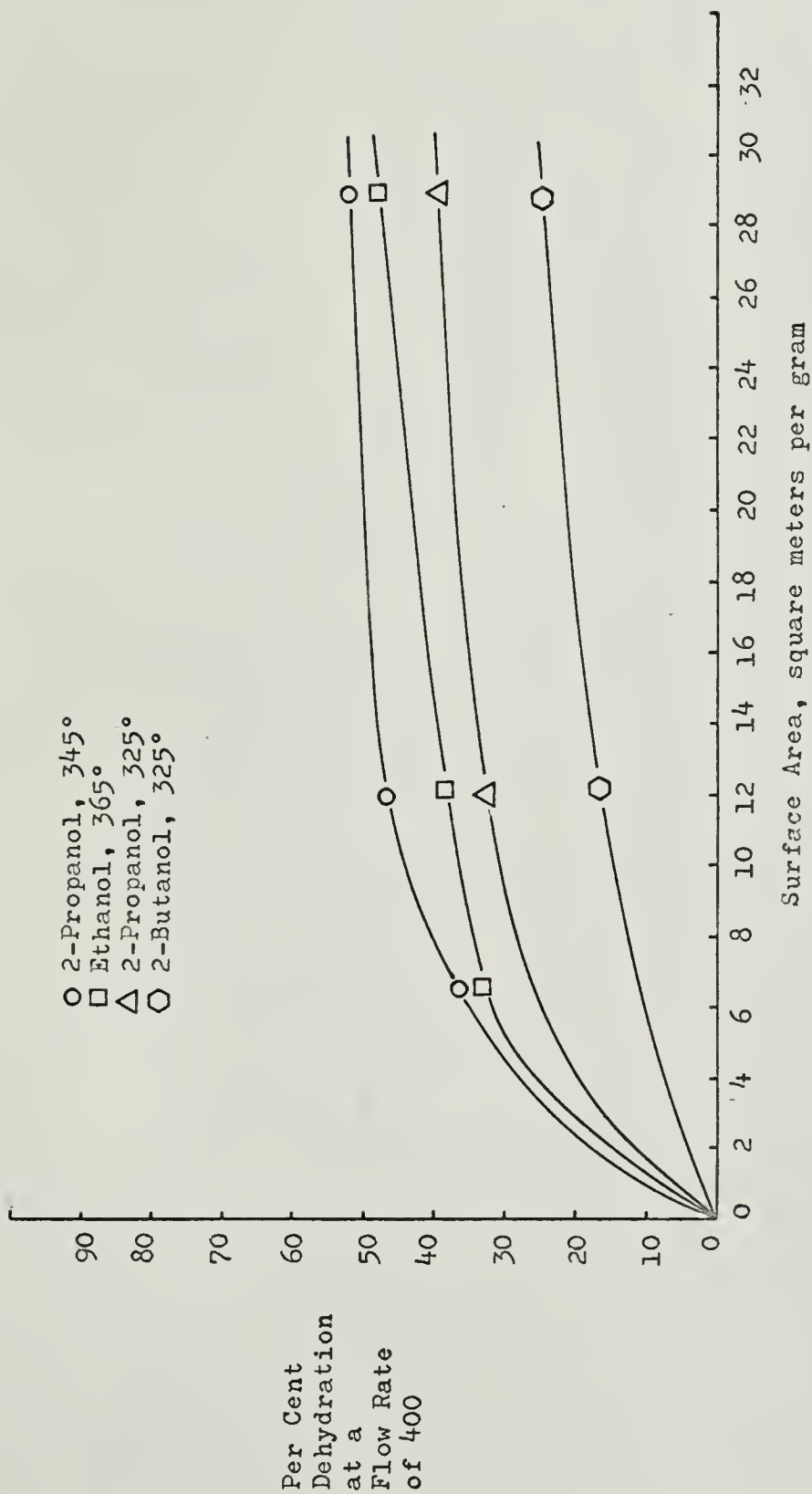


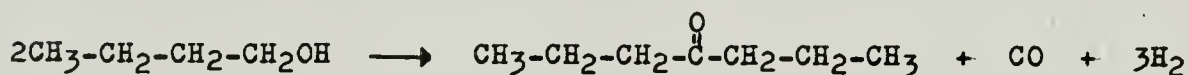
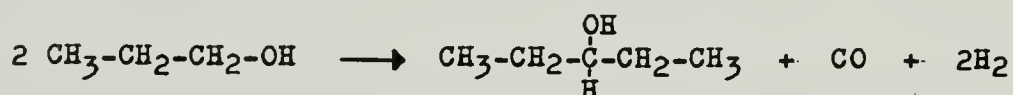
Figure 7. Dehydration of secondary alcohols as a function of catalyst surface area

The measured dehydrogenation of 2-propanol was greater over catalyst V than over either II or VI; dehydrogenation of 2-butanol was also greater over V than over VI. This appears to suggest that the dehydrogenation of these alcohols increases with surface area to a point, then decreases with further surface area increase. More experiments need to be done to verify this, but it can be stated with a reasonable degree of certainty that, at the least, dehydrogenation of these two alcohols does not increase with surface area as rapidly as does dehydration.

### 3. Other reactions of 1-propanol and 1-butanol

The reaction of 1-propanol to yield 3-pentanol and of 1-butanol to yield 4-heptanone was somewhat surprising. Although a number of investigators (16) (17) have reacted acids over thorium to obtain ketones and esters, no report has been found in the literature of the production of these compounds from alcohols.

The net reactions producing these products were determined to be



An effort was made to detect 3-pentanone in 1-propanol reaction products and 4-heptanone in 1-butanol reaction products. Although there was a small amount of high boiling material in the 1-butanol products which may have been 4-heptanol (it appeared to be an alcohol and the boiling point was in the right vicinity),

no positive identification was made. No trace of 3-pentanone was found.

In Figure 8 are plotted representative results of the production of 3-pentanol from 1-propanol and 4-heptanone from 1-butanol. Catalyst V was more effective in the production of these compounds than catalyst VI, the same relationship as that found for the dehydrogenation of the secondary alcohols.



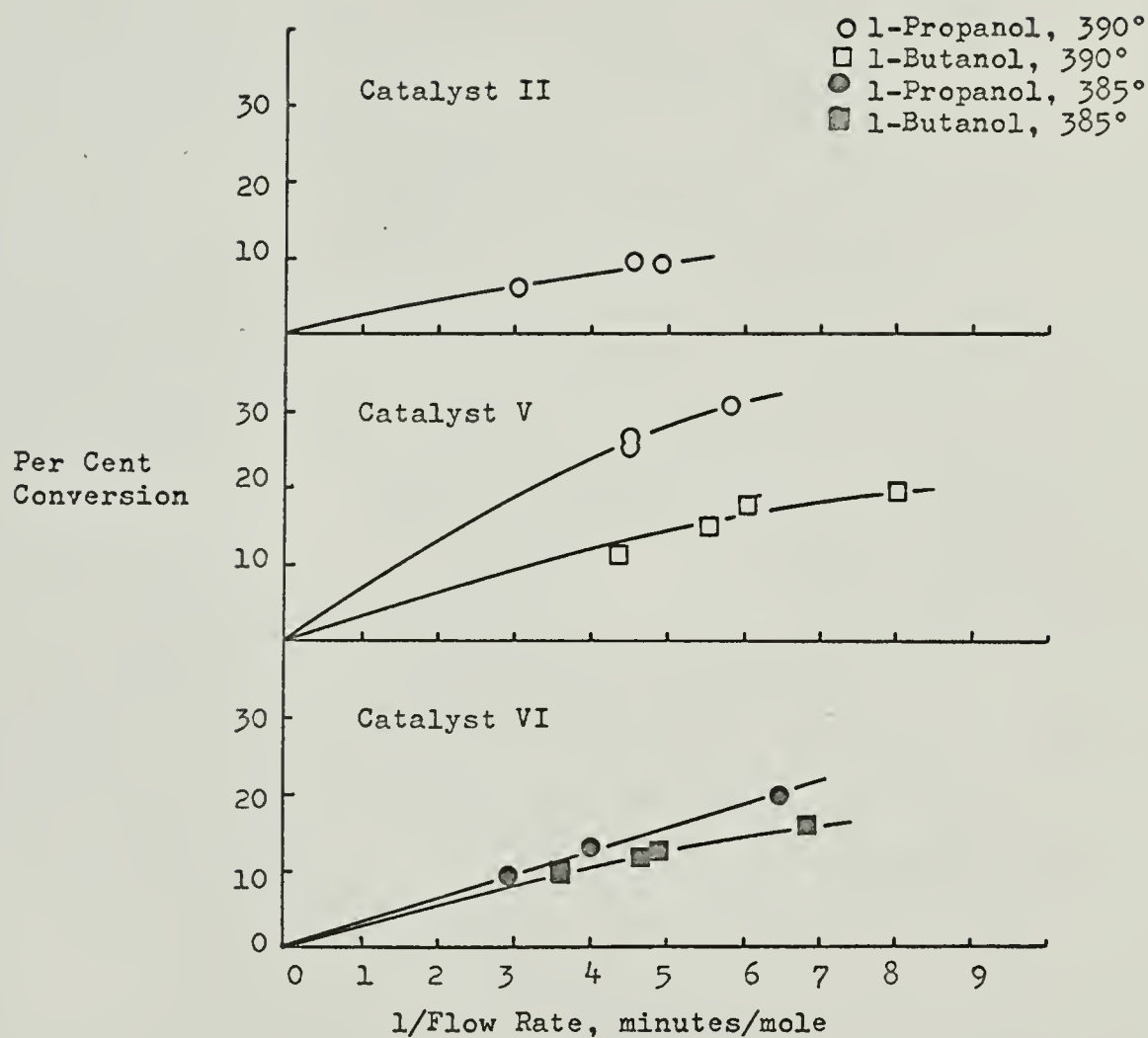


Figure 8. Conversion of 1-propanol to 3-pentanol and 1-butanol to 4-heptanone as a function of reciprocal flow rate

#### IV. DISCUSSION OF RESULTS AND CONCLUSIONS

In Chapter I it was pointed out that thoria effects both dehydration and dehydrogenation of alcohols. The evidence seems strong that these two reactions take place on different sites. This appears to be supported by the work done with 2-propanol and 2-butanol in the present investigations. The conversion to water and olefin was shown to increase with an increase in surface area; after an initial increase with surface area, per cent dehydrogenation appeared to decrease with an increase in surface area, a trend opposite to that of dehydration.

A point made in Chapter III was that per cent dehydration of ethanol, as well as the other alcohols, does not increase linearly with surface area; that is, a doubling of surface area does not cause a doubling of per cent dehydration. A close examination of Figure 6 will show that a linear relationship apparently does exist at very low surface areas, but that this relationship fails as the surface area increases. This means either that the number of sites per square centimeter of surface chemically able to promote dehydration decreases as the surface area increases, the site density decrease being faster than the surface area increase, or that the fraction of the surface accessible to nitrogen molecules but not to ethanol molecules increases with surface area. The latter assumption appears to be more reasonable.

If indeed a large part of the surface is accessible to nitrogen molecules but not to ethanol, this means that there must exist many pores, cracks or crevices of molecular size. It will be recalled that this was one assumption made by Schwab (5) in proposing that dehydration occurs in pores while dehydrogenation occurs on flat surface regions.

The relative dehydration reactivities of the primary alcohols over thoria seems to support Schwab's proposal. Many pores (cracks, crevices, etc.), accessible to ethanol would not be so to the larger molecules, or at least a special configuration of the alcohol molecule would be required for it to enter the pore. The larger the molecule the less likely it would be to get into this configuration and the less likely dehydration would be to occur.

Since the reactivities of the secondary alcohols are in the same order over alumina and thoria, little information is gained from their reactivities relative to each other or to the other alcohols as to the mechanism of dehydration over thoria. It will be assumed that these relative reactivities are primarily a reflection of the chemical nature of the alcohols themselves. Any proposed mechanism, however, would have to allow for this relative reactivity.

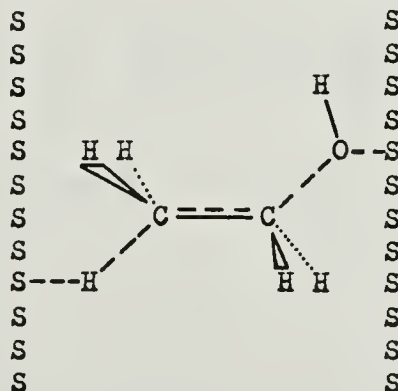
It has been mentioned previously that thoria is quite specific in a number of reactions, differing from alumina in the non-formation of ethers, the specificity of the production of 1-olefins from secondary 2-alcohols and the production of methyl vinyl carbinol instead of methyl ethyl ketone from 2, 3-butanediol. All of this evidence points strongly toward a concerted mechanism for

the dehydration of alcohols over thoria; an ionic mechanism, such as is usually proposed for alumina, would most likely not permit such specificity.

Assuming that, indeed, dehydration does occur in pores by a concerted mechanism one is confronted by two questions: Why do the molecules enter small pores to dehydrate when flat surface is more accessible? And why a concerted mechanism over thoria in contrast to that over alumina?

The following is suggested as a possible mechanism which seems to correlate most of the evidence obtained in the present investigation as well as that of previous investigators.

Most mechanisms for dehydration over alumina (10) involve preliminary removal of the hydroxyl group and then removal of a proton from the resulting carbonium ion. It is suggested that thoria, being less acidic than alumina, is incapable of promoting such a mechanism. The elements of water are eliminated from the alcohol only if the olefin is formed at the same time. The intermediate, as illustrated below, would have half-formed bonds from the catalyst to both the hydroxyl group and the hydrogen to be lost, a half-formed  $\pi$  bond between two alcohol carbons and half-broken carbon-oxygen and carbon-hydrogen bonds.



There appears to be no opportunity for ether formation. In 2, 3-butanediol dehydration, water is removed from one end of the molecule while the double bond is being formed, with the other end of the molecule unaffected, leaving methyl vinyl carbinol.

But why does the dehydration have to be in a pore? One possible explanation is that the stereochemistry of the intermediate is such as to require a pore for the elimination of water. The original idea of Schwab was that the hydroxyl group was attached to one side of a pore while the hydrogen to be lost was attached to the other side. An analysis using molecular models shows that if the oxygen of ethanol is attached to one side of the pore and a hydrogen from the methyl group is attached to the other side in such a way that a straight line can be drawn from the center of the attached hydrogen through the center of the carbon-carbon bond to the center of the oxygen (the hydroxyl group is staggered between two methyl hydrogens), then the centers of the other four hydrogens and the center of the carbon-carbon bond all lie in a plane. This situation seems quite favorable for the formation of ethylene.

The larger alcohols can attach in the same way in the same size pore, but only if the molecule has a rather special configuration. Thus ethanol should be considerably more reactive than the other primary alcohols, and the larger the alcohol molecule the less likely it is to arrange itself in just the correct configuration.

The specificity of production of 1-butene from 2-butanol and the reactivities of the secondary alcohols relative to the



primary alcohols can be explained by allowing two more assumptions, that the oxygen is bonded more readily to the catalyst surface than any of the hydrogens and that there are many more adsorptions than there are dehydrations.

In 2-butanol there are three hydrogens on carbon number one, and two on carbon number three. For a concerted mechanism this reduces the chances for the production of 2-butene. Furthermore, an analysis with molecular models shows that only one of these would be at all likely to attach so as to be eliminated in dehydration; attachment of the other in a straight-line relationship would require such a bending of the molecule that it could no longer fit in the pore. If it is assumed that the oxygen is attached to the surface of the pore first, one can picture the molecule twisting itself until a hydrogen is attached in just the right position to allow elimination of water. The methyl group alpha to the hydroxyl carbon could spin quite freely while the rest of the molecule would be restricted in its movement by the sides of the pore. The probability is quite high that one of the methyl hydrogens would attach in the correct position before the one eligible methylene hydrogen. Thus, the probability of the production of 2-butene is extremely low.

In assuming that many adsorptions do not result in dehydrations, one allows the chemical differences of the secondary and primary alcohols to explain the differences in reactivities. With a free-spinning methyl group next to the hydroxyl carbon, the secondary 2-alcohols can attach in the straight-line relationship almost as readily as ethanol, and a larger percentage of these adsorptions result in elimination of water.

Dehydrogenation presumably occurs in a manner similar to that over ordinary dehydrogenation catalysts, by a mechanism reminiscent of Balandin's hypothesis (1). The two hydrogens to be eliminated are adsorbed on the surface adjacent to each other. As the carbon-hydrogen and oxygen-hydrogen bonds are broken, the hydrogen-hydrogen bond is formed. The decrease in dehydrogenation in going from catalyst V to VI can be explained either by a loss in flat surface available for dehydrogenation, or by the fact that a higher degree of dehydration left less alcohol for dehydrogenation. Perhaps a combination of these factors was involved.

No fully adequate explanation has been found for the production of 3-pentanol from 1-propanol and 4-heptanone from 1-butanol. Previous investigations (16) (17) with acids over thoria have indicated that apparently salts are formed with the catalyst surface, then carbon dioxide is eliminated between two salt molecules. In the same manner, one mechanism for the production of 4-heptanone from 1-butanol would involve the adsorption with elimination of hydrogen of two molecules of propanol, formed from dehydrogenation of the alcohol, on adjacent sites. The carbonyl carbon would be attached to an oxygen of the catalyst, forming a sort of salt molecule. The two molecules would then eliminate carbon monoxide between them, forming 4-heptanone. Elimination of carbon monoxide from adjacently-adsorbed 1-propanol and propanal could form 3-pentanol. The existence of small amounts of the appropriate aldehyde in products from these reactions seems to favor a mechanism involving initial production of the aldehyde. However, additional evidence is needed before any real conclusions can be drawn.



From Figure 8 it can be seen that catalyst V was more active in the production of 3-pentanol and 4-heptanone than catalyst VI. This difference in activity could possibly reflect a loss in activity of catalyst VI with use; it is recalled that the dehydration activity of catalyst VI decreased with use. However, the dehydration of the secondary alcohols was greater over VI than over V, while the dehydrogenation was less. This suggests that perhaps dehydrogenation and production of 3-pentanol and 4-heptanone occur on the same type of site. Since the bimolecular reaction almost certainly occurs on a relatively flat surface, the results appear to give some support to the proposal that dehydrogenation occurs on flat surfaces.

No mention has been made of the type of bonding occurring between adsorbed alcohol molecules and the catalyst surface. Although this point is obviously important, little is actually known of this and any discussion, although interesting, is little more than speculation.

It appears likely that the hydrogen to be lost is bonded to an oxygen on the surface. This oxygen could be part of the thorium oxide lattice or part of a water molecule bonded to the surface. In dealing with thorium, one should consider the possibility of complex formation. The oxygen from an alcohol molecule could complex with a thorium atom on the surface upon dehydration. Probably more likely, however, is that the removal of the hydroxyl group is effected through water already on the surface, possibly complexed with the thorium.

Another point to consider is that active sites could possibly be the result of chemical abnormalities of some type. These might be defects common to the crystal as a whole or chemical peculiarities produced by the very existence of a surface.

Colored samples of thoria (usually blue or blue-green) which have been prepared suggest the possibility of the existence of unpaired electrons. Thorium oxide catalysts prepared by calcining the oxalate are usually more catalytically active than those prepared from the hydroxide. Although a higher surface area can explain the higher activity to some extent, one should consider the distinct possibility of lattice defects due to incomplete removal of carbon and the existence of oxidation states of thorium other than four. Further work is planned in this laboratory in an attempt to obtain information as to the existence and nature of these chemical abnormalities in thoria.

Complicating the whole area of heterogeneous catalysis is the fact that the environment on the catalyst surface during catalytic reactions is quite different from that during most other investigations of the nature of the surface. Thus, more catalytic reaction investigations are desirable, in addition to investigations as to the nature of the fresh surface.

At the outset of the investigations described herein, the intention was to obtain kinetic data from the reactions of one or two alcohols over thoria and to determine the effect of catalyst surface area on these reactions. When it was found that a decrease in catalyst activity prevented the reproducibility of results to the exactitude necessary for reliable determination of kinetic

constants, it was decided to perform the investigations as to the effects of the variation of alcohol molecular size. These have proved fruitful in leading to the proposal as to the mechanism of alcohol dehydration over thoria and in the discovery of a type of reaction heretofore unreported in the literature. The results indicate a need for investigations with still other alcohols. If the problem of catalytic activity decrease can be solved, exact kinetic investigations should prove fruitful.

In the present investigations it has been assumed that a difference in activity from one catalyst to the other was due to a change in the area of the surface available for reaction. It is entirely possible, however, that some other property of the catalysts, which is proportional to the surface area for the catalysts investigated, is responsible for the change in catalytic activity. Correlations should be attempted between catalytic activity and other properties of the catalyst, such as lattice defects, after techniques for the determination of these properties are developed.

Quite recent investigations (7) have resulted in the preparation of catalysts with surface areas around 100 square meters per gram, very high for thorium oxide. The comparison of reactions over these catalysts to those over low surface area catalysts should prove quite interesting.

## V. SUMMARY

Six thorium oxide catalysts have been prepared by the precipitation of thorium hydroxide from thorium nitrate solution with ammonia. The hydroxide was dried, pelleted and heated under vacuum at 600° for four to twenty-nine hours. The surface area of each of the catalysts has been measured.

The products of the reactions of ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol over thoria have been separated and identified. Each of the alcohols dehydrated to produce water and the appropriate olefin; 2-butanol produced 1-butene but no 2-butene. 2-Propanol and 2-butanol lost hydrogen to produce acetone and methyl ethyl ketone, respectively. 1-Propanol and 1-butanol both reacted to lose carbon monoxide and hydrogen; in the process 3-pentanol was formed from 1-propanol and 4-heptanone from 1-butanol.

The tendency to dehydrate has been found to be 2-propanol > 2-butanol > ethanol >> 1-propanol > 1-butanol.

An increase in catalyst surface area caused a considerable but non-linear increase in the dehydration of ethanol, 2-propanol and 2-butanol, but little increase in the dehydration of 1-propanol and 1-butanol.

These results have led to a proposal, similar to that of Schwab's that dehydration occurs by the concerted elimination of

water in pores. The alcohol molecule is proposed to attach to the pore walls in such a way as to make favorable formation of the olefin. The mechanism permits the explanation of four peculiarities of thoria as a dehydration catalyst: (a) the non-formation of ethers, (b) the preferential formation of 1-olefins from secondary 2-alcohols, (c) the production of methyl vinyl carbinol from 2, 3-butanediol and (d) the greater dehydration reactivities of alcohols of smaller size.



## APPENDIX

### Some Details of the Analyses of Reaction Products

#### A. Qualitative

Water, a reaction product of all the alcohols, was identified by chromatographic retention times under various conditions (or by increase in peak size with addition of water) and by the characteristic peak shape on a chromatogram.

Schmidt (12) identified acetone and water as the two condensable 2-propanol products from reactions under conditions almost identical to those in this investigation. He distilled the products, obtained infrared spectra, and prepared derivatives of the component suspected of being acetone. In view of this, the only identification of acetone felt necessary was the verification of retention times with that of the known. Methyl ethyl ketone, a product of 2-butanol in a reaction analogous to that of 2-propanol, was also identified from retention times.

The identification of compounds by chromatographic retention times leaves some room for doubt, in that two different components could possibly have the same retention times and produce the same shape peak. However, the column packing material was designed to separate components which would be expected from alcohol reactions. In the absence of evidence to the contrary, it was assumed that only simple dehydration and dehydrogenation were occurring with ethanol, 2-propanol, and 2-butanol.

The identification of 3-pentanol and 4-heptanone, the only products other than water from 1-propanol and 1-butanol, was done as described in section III-A.

## B. Quantitative

### 1. Determination of per cent dehydration of ethanol

Samples of known solutions of ethanol and water, prepared by weighing the two components, were put through the chromatograph. The areas of the peaks on the resulting chromatogram were determined with a planimeter. Plots were then made of the per cent contributed by water of the total area of the two peaks against the mole per cent water in the mixture, and of the peak area per cent against weight per cent.

Samples of reaction mixtures were put through the chromatograph and peak area percentages determined. From the calibration curves the mole per cent water in the mixture could be determined. Since one mole of ethanol will produce one mole of water upon dehydration, the mole per cent water in the mixture could be taken as the mole per cent conversion.

Periodic mole balance calculations were made, but, since the method described above gave consistent results, the actual number of moles of product was not calculated for each run. The following data give examples of mole balance calculations of two runs with ethanol.

	Run No. 156	Run No. 159
(a)	0.261	0.247
(b)	0.103	0.088



	Run No. 156	Run No. 159
(c) Moles unreacted alcohol	0.166	0.167
(d) Water plus unreacted alcohol	0.269	0.255
(e) Grams liquid product	9.50	9.27
(f) Moles gas	0.082	0.075
(g) Conversion (curves)	38.5%	36.5%
(h) Conversion (liquid)	39.5%	35.6%
(i) Conversion (gas)	31.4%	30.4%

The number of moles of feed was calculated by multiplying the volume of alcohol feed times the known density at the temperature of the reservoir and dividing by the molecular weight. The number of moles of water and unreacted alcohol ( (a) and (c) above) were determined by multiplying the grams of liquid product by the appropriate weight fraction as obtained from peak area percentages and calibration curves. Trials with nitrogen, at pressure differentials the same as those experienced during reaction, indicated that the true volume of gas passing through the Wet Test Meter was very nearly three-fourths of the reading indicated. This factor was used when calculating the number of moles of gas produced.

The mole per cent conversion (g) was determined from the calibration curves as described above. The conversion (h) was calculated by dividing the number of moles of water by the moles of feed, and (i) was determined by dividing the number of moles of gas by the moles of feed.

It is apparent that the simpler determination of mole per cent of water using the calibration curves directly is as satisfactory as calculating the number of moles of water produced and the conversion from this.

Since some of the gas, assumed to be all ethylene, dissolved in the liquid products, the number of moles of gas was always less than that of water, but close enough to serve as a convenient check.

## 2. Calculation of three-component mixtures; 2-propanol determinations

The calculation of the mole percentages of acetone, 2-propanol and water in a mixture of these will be considered as an example of the method used to determine relative amounts of components in a reaction mixture.

Calibration curves (area per cent vs. mole per cent and area per cent vs. weight per cent) were made from determinations of known solutions of water and 2-propanol. The fraction of water in the mixture containing acetone was obtained from these curves as if the non-water peak area on the chromatogram was all alcohol. Since peak areas are proportional to weight, this will hold quite well in any mixture if the component other than alcohol and water has a molecular weight close to that of the alcohol, or if this component is present in small amounts.

For convenience the following symbols will be adopted:

2P = 2-propanol	m = number of moles of ...
Ac = acetone	wt = weight of ...
H <sub>2</sub> O = water	mw = molecular weight of ...

Assuming area ratios to be equal to weight ratios:

$$\frac{m \text{ Ac}}{m \text{ 2P}} = \frac{wt \text{ Ac}}{wt \text{ 2P}} \times \frac{mw \text{ 2P}}{mw \text{ Ac}} = \frac{\text{area \% Ac}}{\text{area \% 2P}} \times \frac{mw \text{ 2P}}{mw \text{ Ac}} \quad (i)$$

$$m_{Ac} = \frac{\text{area \% Ac}}{\text{area \% 2P}} \times \frac{mw_{2P}}{mw_{Ac}} \times m_{2P} = K \times m_{2P} \quad (ii)$$

Assuming, for convenience, a total of 100 moles:

$$m_{Ac} + m_{2P} = 100 - m_{H_2O} \quad (iii)$$

Substituting  $m_{Ac}$  from (ii) and  $m_{H_2O}$  obtained from the calibration curves, and solving for  $m_{2P}$ , one obtains

$$m_{2P} = \frac{100 - m_{H_2O}}{1 + K} \quad (iv)$$

which is then also equal to the mole per cent 2-propanol in the mixture.

The results of the application of this method to one known mixture are given below:

	Per cent determined by weight		Calculated per cent	
	weight per cent	mole per cent	area per cent	mole per cent
Acetone	8.1	6.6	7.5	6.4
2-Propanol	81.4	65.3	81.1	66.6
Water	10.5	28.0	11.4	27.0

Although the figures are given to the nearest tenth per cent, the error in determination of the peak areas prevents such precision in most measurements. The calculations listed are probably somewhat more accurate than those for an average reaction product determination.

An example of the results of mole balance checks of 2-propanol products is given below; the calculations are for run number 37.

(a) Moles feed	0.134
(b) Moles water	0.046
(c) Moles acetone	0.003
(d) Moles unreacted alcohol	0.095
(e) Grams liquid product	6.81
(f) Moles gas	0.009
(g) Dehydration (curves)	38.7%
(h) Dehydration (liquids)	34.3%
(i) Dehydrogenation (calculated)	3.0%
(j) Dehydrogenation (liquid)	2.3%
(k) Dehydrogenation (gas)	6.7%

The number of moles of feed was determined in the same way as for ethanol. The moles of water, acetone and unreacted alcohol in the liquid products were calculated by multiplying the weight of these products by the appropriate weight fraction, determined as described above.

The dehydration figure (g) and dehydrogenation figure (i), those listed in Table II, were determined as described above. The figures (h) and (k) were obtained by dividing the calculated number of moles of water and of acetone in the liquid products by the number of moles of feed.

The dehydrogenation figure (k) was obtained by dividing the number of moles of gas by the moles of feed, assuming all of the gas to be hydrogen. Because of its high volatility, even at dry ice temperatures, some propylene most likely was not trapped out. This probably accounts for the high figure for (k) compared to (i) and (j).

### 3. 1-Propanol determinations

The results of a mole balance check of run number 39 with 1-propanol are as follows:

(a) Moles feed	0.139
(b) Grams liquid product	6.68
(c) Moles water	0.026
(d) Moles 3-pentanol	0.009
(e) Moles unreacted alcohol	0.095
(f) Moles gas	0.049
(g) Dehydration (curves)	23%
(h) Dehydration (liquid)	19%
(i) Conversion to 3-pentanol (calculated)	18%
(j) Conversion to 3-pentanol (liquid)	13%
(k) Conversion to 3-pentanol (gas)	23%

The number of moles of feed, water and 3-pentanol were determined in the same manner as for the three components in 2-propanol liquid products.

The dehydration figure (g) and conversion figure (i) were calculated by the method described above for a three-component mixture. The dehydration figure (h) was calculated by dividing (c) by (a). Since two moles of alcohol were needed to produce one of 3-pentanol, the figure (j) was obtained by dividing (d) by (a) and doubling.

The conversion figure (k) was obtained by multiplying the number of moles of gas by two-thirds, since three moles of gas (two of hydrogen and one of carbon monoxide) were produced for every two moles of 1-propanol converting, and dividing by the moles of feed. Since an unknown amount of propylene was included in the gas volume measured, this figure is probably somewhat too high, as comparisons with (i) and (j) indicate. This figure is listed in Table III, however, since the data calculated this way were much more precise and probably as accurate as that calculated



from chromatograms. The water peak on the chromatogram tailed into the 3-pentanol peak slightly. This affected the water peak little, but made the determination of the base line of the 3-pentanol peak somewhat uncertain. Since this peak was low and long, a shift in baseline caused a considerable change in peak area.

#### 4. 2-Butanol determinations

The ease of separation of 2-butanol products affords an opportunity to cross-check the analytical methods.

Since 1-butene has a boiling point of  $-5^{\circ}$ , practically all of it was trapped out. The volume of that trapped in the second collection flask was measured at its boiling point, and the number of moles calculated from the known density at this temperature and the molecular weight. The weight dissolved in the liquid products was determined from the peak areas of a chromatogram, allowing the same assumptions as with a 2-propanol mixture. This afforded a direct check on dehydration as determined in the manner previously described.

Since practically all products were trapped out as liquids except hydrogen, the gas volume afforded a direct check on dehydrogenation as determined by obtaining the amount of methyl ethyl ketone produced.

The results of a mole balance check of run number 26 are as follows:

(a) Moles feed	0.119
(b) Grams liquid product	8.37
(c) Moles water	0.016
(d) Moles methyl ethyl ketone	0.002
(e) Moles unreacted alcohol	0.107

(f) Moles dissolved 1-butene	0.013
(g) Moles trapped 1-butene	0.003
(h) Moles gas	0.002
(i) Dehydration (curves)	15%
(j) Dehydration (liquid)	13%
(k) Dehydration (1-butene)	14%
(l) Dehydrogenation (calculated)	2.5
(m) Dehydrogenation (liquid)	1.8
(n) Dehydrogenation (gas)	1.8

The determination of figures (a), (c), (d), (e) and (f) was done as described previously, from chromatographic peak areas.

The dehydration figure (i) was determined from peak areas and calibration curves, as described previously. The dehydration figure (j) was obtained by dividing the number of moles of water by the moles of feed, and the figure (k) was obtained by dividing the number of moles of 1-butene by the moles of feed.

Dehydrogenation figure (l) was obtained by determining the mole per cent methyl ethyl ketone in the same way that acetone was determined in 2-propanol mixtures. The figures (m) and (n) were obtained by dividing the moles of methyl ethyl ketone and hydrogen, respectively, by the moles of feed.

##### 5. 1-Butanol determinations

The results of a mole balance check of run number 18 are as follows:

(a) Moles Feed	0.128
(b) Grams liquid product	8.37
(c) Moles water	0.019
(d) Moles 4-heptanone	0.009
(e) Moles unreacted alcohol	0.107
(f) Moles dissolved 1-butene	0.009
(g) Moles trapped 1-butene	0.009
(h) Moles gas	0.037
(i) Dehydration (curves)	18%
(j) Dehydration (liquid)	15%
(k) Dehydration (1-butene)	14%
(l) Conversion to 4-heptanone (calculated)	17%
(m) Conversion to 4-heptanone (liquid)	14%
(n) Conversion to 4-heptanone (gas)	14%



The determinations of (a), (c), (d), (e) and (f) were done as described previously.

The dehydration per cent (i) was determined from peak areas and calibration curves. The dehydration per cent (j) was obtained by dividing (c) by (a), and the per cent (k) was obtained by dividing the total number of moles of 1-butene by (a).

The conversion to 4-heptanone (l) was calculated by determining the mole per cent 4-heptanone in the same way that acetone was determined in 2-propanol mixtures and doubling this percentage. The conversion (m) was obtained by dividing (d) by (a) and doubling. Since four moles of gas (one of carbon monoxide and three of hydrogen) were produced for every two moles of 1-butanol converting to 4-heptanone, (h) was halved and divided by (a) to obtain (n).

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## BIOGRAPHICAL SKETCH

John Wallis Legg was born September 20, 1936, in Minter City, Mississippi. After attending the public schools in Drew, Mississippi, he entered Mississippi College, Clinton, Mississippi, in September, 1954, and graduated in May, 1958, receiving the degree of Bachelor of Science, with special distinction.

In September, 1958, Mr. Legg entered the Graduate School of the University of Florida. He held graduate and research assistantships until he received the degree of Master of Science in August, 1960.

From September, 1960, until May, 1962, he held the position of Assistant Professor of Chemistry at Mississippi College, Clinton, Mississippi.

In June, 1962, Mr. Legg re-entered the University of Florida Graduate School and has held a research assistantship since that time.

He is a member of the American Chemical Society, Alpha Chi Sigma and Omicron Delta Kappa.

He is married and has two children.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 19, 1964

E. Rufin Jones  
Dean, College of Arts and Sciences

\_\_\_\_\_  
Dean, Graduate School

Supervisory Committee:

W. B. [unclear]  
Chairman  
R. D. [unclear]  
E. E. Muschitz, Jr.  
P. J. Harrison  
Lehmann

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